PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification** 5 :
B41C 1/055, B41M 5/40 A1

(11) **International Publication Number:** **WO 94/18005**

(43) **International Publication Date:** 18 August 1994 (18.08.94)

(21) **International Application Number:** PCT/EP94/00118

(22) **International Filing Date:** 14 January 1994 (14.01.94)

(30) **Priority Data:**
93200342.9 9 February 1993 (09.02.93) EP
(34) Countries for which the regional or international application was filed: DE et al.

(81) **Designated States:** JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE)

Published
With international search report.

(71) **Applicant** *(for all designated States except US)*: AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP [BE/BE]; Septestraat 27, B-2640 Mortsel (BE).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: VERBURGH, Yves [BE/BE]; Agfa-Gevaert N.V., DIE 3800, Septestraat 27, B-2640 Mortsel (BE). VAN DEN BERGH, Rudolf [BE/BE]; Agfa-Gevaert N.V., DIE 3800, Septestraat 27, B-2640 Mortsel (BE). DE MEUTTER, Stefaan, Karel [BE/BE]; Agfa-Gevaert N.V., DIE 3800, Septestraat 27, B-2640 Mortsel (BE). VERMEERSCH, Joan, Triphon [BE/BE]; Agfa-Gevaert N.V., DIE 3800, Septestraat 27, B-2640 Mortsel (BE).

(54) **Title:** HEAT MODE RECORDING MATERIAL AND METHOD FOR MAKING A LITHOGRAPHIC PRINTING PLATE THEREWITH

(57) **Abstract**

The present invention provides a heat mode recording material having a high recording speed comprising on a support having an ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than $3\mu m$. There is further provided a method for making a printing plate of high quality therewith.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

HEAT MODE RECORDING MATERIAL AND METHOD FOR MAKING A LITHOGRAPHIC PRINTING PLATE THEREWITH.

DESCRIPTION

1. Field of the invention.

The present invention relates to a heat mode recording material for making a lithographic plate for use in lithographic printing. The present invention further relates to a method for imaging said heat mode recording material e.g. by means of a laser.

2. Background of the invention.

Lithographic printing is the process of printing from specially prepared surfaces, some areas of which are capable of accepting ink (hydrophobic areas) whereas other areas will not accept ink (hydrophilic areas). According to the so called conventional or wet printing plates, both water or an aqueous dampening liquid and ink are applied to the plate surface that contains hydrophilic and hydrophobic areas. The hydrophilic areas will be soaked with water or the dampening liquid and are thereby rendered oleophobic while the hydrophobic areas will accept the ink.

When a laser heat mode recording material is to be used as a direct offset master for printing with greasy inks, it is necessary to have hydrophobic-hydrophilic mapping of the image and non-image areas. In the case of heat mode laser ablation it is also necessary to completely image wise remove a hydrophilic or hydrophobic topcoat to expose the underlying hydrophobic respectively hydrophilic surface of the laser sensitive recording material in order to obtain the necessary difference in ink-acceptance between the image and non-image areas.

For example DE-A-2448325 discloses a laser heat mode "direct negative" printing plate comprising e.g. a polyester film support provided with a hydrophilic surface layer. The disclosed heat mode recording material is imaged using an Argon laser thereby rendering the exposed areas hydrophobic. An offset printing plate is thus obtained which can be used on an printing press without further processing. The plate is called a "direct negative" plate because the areas of the recording material that have been exposed are

rendered ink accepting.

Other disclosures in DE-A-2448325 concern "direct negative" printing plates comprising e.g. hydrophilic aluminium support coated with a water soluble laser light (Argon-488nm) absorbing dye or with a coating based on a mixture of hydrophilic polymer and laser light absorbing dye (Argon - 488nm). Further examples about heat mode recording materials for preparing "direct negative" printing plates include e.g. US-A-40341183, DE-A-2607207, DD-A-213530, DD-A-217645 and DD-A-217914. These documents disclose heat mode recording materials that have on an anodized aluminium support a hydrophilic layer. The disclosed heat mode recording materials are image-wise exposed using a laser. Laser exposure renders the exposed areas insoluble and ink receptive, whereas the non exposed image portions remain hydrophilic and water soluble allowing to be removed by the dampening liquid during printing exposing the hydrophilic support. Such plates can be used directly on the press without processing.

DD-A-155407 discloses a laser heat mode "direct negative" printing plate where a hydrophilic aluminum oxide layer is rendered oleophilic by direct laser heat mode imaging. These printing plates may also be used on the press without further processing.

From the above it can be seen that a number of proposals have been made for making a 'direct negative' offset printing plate by laser heat mode recording. They have such disadvantages as low recording speed and/or the obtained plates are of poor quality.

3. Summary of the invention

According to the present invention it is an object to provide an alternative heat mode recording material of high sensitivity for making a negative working lithographic printing plate of high quality.

For ecological reasons it is another object of the present invention that this lithographic printing plate of high quality preferably can be obtained by development under essential dry conditions or with plain water or by using the imaged non processed plate directly on the press, these processing methods are referred to as 'ecological processing'.

Still further objects of the present invention will become clear from the description hereinafter.

According to the present invention there is provided a heat mode recording material comprising on a support having a ink receptive

surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3µm.

According to the present invention there is provided a method for making a lithographic printing plate comprising the steps of:

- image wise exposing a heat mode recording material comprising on a support having a ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3µm and
- subsequently removing said hardened hydrophilic surface layer at the exposed areas by rubbing a thus obtained image-wise exposed heat mode recording material under essentially dry conditions or by using water or an aqueous solution.

4. Detailed description of the invention.

It has been found that in accordance with the present invention negative working lithographic printing plates can be obtained having a high recording speed, yielding a high printing endurance, high sharpness, good contrast and an excellent resolution in an ecologically more acceptable way.

To obtain the effects of the present invention it is important that the thickness of the hydrophilic surface layer is not more than 3µm preferably not more than 1µm. When the thickness of the hydrophilic surface layer becomes more than 3µm a heat mode recording material will be obtained having a low recording speed and yielding printing plates of poor quality. The minimum thickness of the surface layer is not particularly critical but is preferably more than 0.05µm. A particularly interesting range for the thickness of the hydrophilic surface layer is between 0.05µm and 0.5µm.

In order to obtain good lithographic printing properties, especially to obtain a good printing endurance, it is also a requirement that the hydrophilic surface layer be hardened.

According to a preferred method of the present invention the heat mode recording material is image-wise exposed using a laser. Preferably used lasers are e.g. semiconductor lasers, YAG lasers e.g. Nd-YAG lasers, Argon lasers, etc.. The laser may have a power output between 4[illegible] mW and 10[illegible] mW and preferably operates in the infrared part of the spectrum.

Subsequent to the image-wise exposure the hydrophilic surface layer is removed at the exposed imaged areas. Removing can be done by e.g. rubbing using e.g. a brush or a cotton pad. Such rubbing may be carried out during image-wise exposure as described in US-P-5.148.746. Rubbing of the heat mode recording material is preferably carried out in absence of a liquid in essentially dry conditions. However plain water or a water based developer may be used also. Removing the hydrophilic surface layer on the imaged areas can further be done by ultrasonic treatment of the imaged recording material immersed in plain water or a water based developer, by means of a pressure jet of plain water or a water based developer. Removal of the exposed areas may also be done by directly mounting the plate on a printing machine so that the dampening liquid dissolves and removes the hydrophilic surface layer at the exposed areas during startup of the printing machine.

The substance capable of converting light into heat may be present in the support and/or in a separate recording layer provided between the support and the hardened hydrophilic surface layer. The thickness of such a separate recording layer may be varied over a wide range. However when the thickness of such recording layer becomes more than 3µm image-wise exposure should then be carried out through the hardened hydrophilic surface layer. In this case it also preferred not to include an additional layer between such recording layer and the hardened hydrophilic surface layer or to keep the thickness of such additional layer to a minimum preferably not more than 0.5µm. Furthermore when using a recording layer having a thickness of more than 3µm such layer should then be ink receptive.

On the other hand when the thickness of the recording layer is less than 3µm exposure can take place through the support, when transparent, or through the hardened hydrophilic layer. Further in this case the recording layer will generaly not be required to be ink receptive as long as the underlying surface or layer is ink receptive and total removal of the recording layer together with the hydrophilic surface layer at the exposed areas is possible.

In any case, irrespective of the thickeness of the recording layer, exposure through the hardened hydrophilic surface layer is preferred since it has been found that the printing plates obtained in this way have a better resolution and sharpness.

According to a preferred embodiment of the present invention a recording layer is used having a thickness between 0.01µm and 30µm.

Examples of substances capable of converting light into heat that may be used in connection with the present invention are e.g. carbon black, infrared or near infrared absorbing dyes or pigments, metals such as Bi, Sn, Te etc. or a combination thereof. Suitable infrared dyes are disclosed in e.g. US-4833124, EP-321923, US-4772583, US-4942141, US-4948776, US-4948777, US-4948778, US-4950639, US-4950640, US-4912083, US-4952552, US-5024990, US-5023229 etc.. Suitable infrared pigments are e.g. HEUCODOR metal oxide pigments available from Heubach Langelsheim. When a metal such as e.g. bismuth is used as a heat converting substance the recording layer is preferably a vacuum or vapour deposited metal layer.

According to a particular embodiment of the present invention the recording layer may be a vacuum deposited aluminium layer. The thickness of such an aluminium layer however should be less than 250 Å and more preferably between 100Å and 225Å.

However the substance capable of converting light into heat may alos be dissolved or dispersed in a binder. Polymeric binders for the recording layer are preferably hydrophobic such as e.g. cellulcse esters e.g. cellulose acetate, cellulose nitrate, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, etc.. Preferably the polymeric binder in the recording layer is heat sensitive: e.g. a polymer containing nitrate ester groups (e.g. self oxidizing binder cellulose nitrate as disclosed in GB-1316398 and DE-A-2512038); e.g. a polymer containing carbonate groups (e.g. polyalkylene carbonate); e.g. a polymer containing covalently bound chlorine (e.g. polyvinylidene chloride).

Suitable supports for a heat mode recording material used in connection with the present invention are preferably non-metallic supports having a hydrophobic (ink receptive) surface e.g. a polyester film support, paper coated with a polyolefin such as polyethylene, polycarbonate film, polystyrene film etc.. However metallic support such as e.g. aluminium can also used in connection with the present invention. In case the surface of the support is not or insufficiently hydrophobic it may be provided with an intermediate hydrophobic primer coating whereon a recording layer may be deposited. Alternatively the recording layer can be the hydrophobic layer at the same time.

According to the present invention the recording layer may comprise additional substances such as plasticizers, crosslinking agents and resins, particulate materials such as e.g. polyethylene

or fluorinated polymer dispersions, etc.. to impart toughness, print durability and oleophilic surface characteristics of the ablated image portions of the recording layer, wetting agents, matting agents, anti-oxidizing agents etc.. Preferably the recording layer will be hardened when it includes a binder.

Concerning the composition of an optional undercoat layer any polymeric binder is suitable provided the adherance between the recording layer and the support is thereby improved. It has also been found that when the undercoat layer contains a polymer with heat labile groups (e.g. covalently bound chloride) adjacent to the recording layer the speed of the recording material can be improved as disclosed in EP 92201633.2.

According to the most preferred embodiment of the present invention imaging of the heat mode recording material takes place through the hydrophilic surface layer. In this way excellent image quality (high sharpness, good contrast, excellent resolution) and increased sensitivity are obtained.

Different kinds of hardened hydrophilic surface layers are suitable in connection with the present invention. The hydrophilic coatings are preferably cast from aqueous compositions containing hydrophilic binders having free reactive groups including e.g. hydroxyl, carboxyl, hydroxyethyl, hydroxy-propyl, amino, aminoethyl, aminopropyl, carboxymethyl, etc.. along with suitable crosslinking or modifying agents including e.g. hydrophilic organotitanium reagents, aluminoformyl acetate, dimethylol urea, melamines, aldehydes, hydrolyzed tetraalkyl orthosilicate, etc..

Suitable polymers for hydrophilic layers may be selected from the group consisting of gum arabic, casein, gelatin, starch derivatives, carboxymethyl cellulose and Na salt thereof, cellulose acetate, sodium alginate, vinyl acetate-maleic acid copolymers, styrene-maleic acid copolymers, polyacrylic acids and salts thereof, polymethacrylic acids and salts thereof, hydroxy-ethylene polymers, polyethylene glycols, hydroxypropylene polymers, polyvinyl alcohols, and hydrolyzed polyvinylacetate having a hydrolyzation degree of at least 60% by weight and more preferably at least 80% by weight.

Hydrophilic layers containing polyvinylalcohol or polyvinylacetate hydrolyzed to an extent of at least 60% by weight hardened with a tetraalkyl orthosilicate, e.g. tetraethyl orthosilicate or tetramethyl orthosilicate, as disclosed in e.g. US-P-3476937 are particularly preferred because their use in the present heat mode recording material results in excellent

lithographic printing properties.

A further suitable hardened hydrophilic surface layer is disclosed in EP 92201227.5. The hydrophilic layer disclosed in this EP-application comprises the hardening reaction product of a (co)polymer containing amine or amide functions having at least one free hydrogen (e.g. amino modified dextrane) and aldehyde.

According to the present invention the hardened hydrophilic surface layer may comprise additional substances such as e.g. plasticizers, pigments, dyes etc.. The hardened hydrophilic surface layer may also comprise particulate materials such as e.g. TiO_2 or colloidal silica to increase the strength and/or hydrophilic character of the hydrophilic layer.

The present invention will now be illustrated with the following examples without however limiting it thereto. All parts are by weight unless otherwise specified.

EXAMPLE 1

To a polyethylene terephthalate support provided with a layer of a copolymer of vinylidene chloride (88 mol%), methylacrylate (10 mol%) and itaconic acid (2mol%) in an amount of $170 mg/m^2$ was vacuum deposited a bismuth layer as a recording layer such that the optical density thereof was 4.5 (thickness of about 0.30 µm).

To this recording layer was then coated the following coating dispersion for the hydrophilic layer: to 82 grams of a dispersion containing 21.5 % of TiO2 (average particle size 0.3 to 0.5 µm) and 2.5 % of polyvinylalcohol in deionized water were subsequently added, while stirring, 639 grams of a 5 % polyvinyl alcohol solution in water, 77 grams of a hydrolyzed 22 % tetramethyl orthosilicate emulsion in water and 22 grams of a 10 % solution of a wetting agent. To this mixture was then added 180 grams of deionized water and the pH was adjusted to pH=4. The coating dispersion was coated on the recording layer to a dry thickness of 0.5 µm to obtain a hydrophilic surface layer. After drying at 30°C the thus obtained element was subjected to a temperature of 80°C for several hours.

The thus prepared heat mode recording material was image-wise exposed through the hydrophilic surface layer with a Nd-YLF laser (1053 nm) at a linear writing speed of 32.8 m/s, with a spot diameter of 18 µm (1/e2) and a power output at the surface of the heat recording material of 1000 mW. After imaging the hydrophilic surface layer was image-wise removed by rubbing with a dry cotton

pad to expose the hydrophobic image portions of the support. The optical density of the imaged image portions was decreased to about 0.05 compared to the non imaged areas having an optical density of 4.5. This difference in optical density between imaged and non imaged portions allows visual inspection of the recorded image on the plate.

The printing plate thus prepared was mounted on a printing press ABDick 360 and was used to print with a commonly employed ink and dampening solution. The achieved image-wise hydrophobic-hydrophilic differentiation was satisfactory and print copies of good quality were obtained.

EXAMPLE 2

The imaged heat mode recording material as described in example 1 was image-wise exposed as described in example 1 and subjected to ultrasonic treatment in plain water during 2 minutes.

The printing plate thus prepared was mounted on a printing press ABDick 360 and was used to print with a commonly employed ink and dampening solution. The image-wise achieved hydrophobic-hydrophilic differential was satisfactory and print copies of good quality were obtained.

EXAMPLE 3

The imaged heat mode recording material as described in example 1 was image-wise exposed as described in example 1 and was then mounted without further processing on a printing press ABDick 360. The recording material was used to print with a commonly employed ink and dampening solution. The image-wise achieved hydrophobic-hydrophilic differential was satisfactory and print copies of good quality were obtained.

EXAMPLE 4

To a polyethylene terephthalate support was coated a dispersion for the recording layer having the following composition: 9.5 grams of low molecular weight nitrocellulose E330 (1), 9.5 grams of carbon black Special Schwarz 250, 0.2 grams of Solsperse 5000 (2), 0.8 grams of Solsperse 24000 (3), 80 grams of n-butanone. The recording layer was applied to a dry coating thickness of about 0.5 µm

corresponding to an optical density of about 1.

(1) E330 is a low molecular nitrocellulose, supplier Wolff Walsrode.
(2) Solsperse 5000 is a dispersing agent from ICI.
(3) Solsperse 24000 is a dispersing agent from ICI.

To this recording layer was then coated the coating dispersion from example 1 for the hydrophilic layer to a dry thickness of 0.5 µm to obtain a hydrophilic surface layer. After drying at 30°C the thus obtained element was subjected to a temperature of 80°C for several hours.

The thus prepared heat mode recording material was image-wise exposed through the hydrophilic layer with a Nd-YLF laser (1053nm) at a linear writing speed of 32.8 m/s, with a spot diameter of 18 µm (1/e2) and a power output at the surface of the heat mode recording material of 1600 mW. After imaging the hydrophilic surface layer was image-wise removed by rubbing with a dry cotton pad to expose the hydrophobic image portions of the remaining recording layer. The optical density of the imaged image portions was decreased to about 1 compared to the non imaged areas having an optical density of 2. This difference in optical density between imaged and non imaged portions allows visual inspection of the recorded image on the plate.

The printing plate thus prepared was mounted on a printing press ABDick 360 and was used to print with a commonly employed ink and dampening solution. The achieved image-wise hydrophobic-hydrophilic differentiation was satisfactory and print copies of good quality were obtained.

EXAMPLE 5

To a polyethylene terephthalate support was coated a dispersion for the recording layer according the composition of example 4. The recording layer was applied to a dry coating thickness of about 6 µm corresponding to an optical density of >5.

To this recording layer was then coated the coating dispersion from example 1 for the hydrophilic layer to a dry thickness of 0.5 µm to obtain a hydrophilic surface layer. After drying at 30°C the thus obtained element was subjected to a temperature of 80°C for several hours.

The thus prepared heat mode recording material was image-wise

exposed through the hydrophilic surface layer with a Nd-YLF laser (1053 nm) at a linear writing speed of 32.8 m/s, with a spot diameter of 18μ (1/e2) and a power output at the surface of the heat mode recording material of 1600 mW. After imaging the hydrophilic surface layer was image-wise removed by rubbing with a dry cotton pad to expose the hydrophobic image portions of the remaining recording layer. The image portions showed a decreased optical reflectance compared to the non imaged areas. The difference in optical reflectance between imaged and non imaged portions allows visual inspection of the recorded image on the plate.

The printing plate thus prepared was mounted on a printing press ABDick 360 and was used to print with a commonly employed ink and dampening solution. The achieved image-wise hydrophobic-hydrophilic differentiation was satisfactory and print copies of good quality were obtained.

EXAMPLE 6

To a polyethylene terephthalate support was coated a dispersion for the recording layer according the composition of example 4. The recording layer was applied to a dry coating thickness of 0.5 μm corresponding to an optical density of about 2.

To this recording layer was then coated following coating composition for the hydrophilic surface layer: prior to application was added to 100g of a solution containing 2 % of carboxymethylcellulose (CMC) 4.5 grams of a hydrolyzed 22 % tetramethyl orthosilicate emulsion in water and 2 grams of a 10 % solution of a wetting agent. The pH of the composition was adjusted to pH=4. The coating dispersion was coated on the recording layer to a thickness of 0.5 μm. After drying at 30°C the thus obtained element was subjected to a temperature of 130°c for 5 minutes. After polishing with a wet cotton pad a very though hydrophilic surface layer with a thickness of <0.5 μm was obtained on the hydrophobic nitrocellulose-carbon black based recording layer.

The thus prepared heat mode recording material was image-wise exposed through the hydrophilic toplayer with a Nd-YLF laser (1053 nm) at a linear writing speed of 32.8 m/s, with a spot diameter of 18 μm (1/e2) and a power output at the surface of the heat mode recording material of 1600 mW. After imaging the hydrophilic surface layer was image-wise removed by rubbing with a dry cotton pad to expose the hydrophobic image portions of the remaining recording

layer. The optical density of the imaged portions was about 1 compared to the non imaged areas showing an optical density of 2. This difference in optical density between imaged and non imaged portions allows visual inspection of the recorded image on the plate.

The printing plate thus prepared was mounted on a printing press ABDick 360 and was used to print with a commonly imployed ink and dampening solution. The acchieved image-wise hydrophobic-hydrophilic differentiation was satisfactory and print copies of good quality were obtained.

EXAMPLE 7

The imaged heat mode recording materials prepared and exposed according to examples 4, 5 and 6 were subjected to ultrasonic treatment in plain water during 2 minutes.

The printing plates thus prepared were mounted on a printing press ABDick 360 and were used to print with a commonly used ink and dampening. The image-wise achieved hydrophobic-hydrophilic differential was satisfactory and print copies of good quality were obtained.

EXAMPLE 8

The imaged heat mode recording materials prepared and exposed according to examples 4, 5 and 6 were mounted without further processing on a printing press ABDick 360.

The recording materials were used to print with a commonly employed ink and dampening solution. The image-wise achieved hydrophobic-hydrophilic differential was satisfactory and copies of good quality were obtained.

CLAIMS

1. A heat mode recording material comprising on a support having an ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3µm.

2. A heat mode recording material according to claim 1 wherein said substance capable of converting light into heat is provided in a separate recording layer between said support and said hardened hydrophilic surface layer.

3. A heat mode recording material according to claim 2 wherein said recording layer has a thickness of more than 3µm and is ink receptive.

4. A heat mode recording material according to claim 3 wherein said recording layer is adjacent to said hardened hydrophilic surface layer or wherein there is provided an intermediate layer between said recording layer and said hardened hydrophilic surface layer having a thickness of not more than 0.5µm.

5. A heat mode recording material according to claim 2 wherein the thickness of said recording layer is not more than 3µm.

6. A heat mode recording material according to claim 5 wherein said recording layer is a vapour or vacuum deposited metal layer.

7. A heat mode recording material according to any of the above claims wherein said hardened hydrophilic surface layer comprises the reaction product of a hydrophilic polymer and a hydrolyzed tetraalkyl orthosilicate.

8. A method for making a lithographic printing plate comprising the steps of:
- image-wise exposing a heat mode recording material comprising on a support having a ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3µm and

- subsequently removing said hardened hydrophilic surface layer at the exposed areas by rubbing a thus obtained image-wise exposed heat mode recording material under essentially dry conditions or by using water or an aqueous solution.

9. A method according to claim 8 wherein said substance capable of converting light into heat is provided in a separate recording layer between said support and said hardened hydrophilic surface layer.

10. A method according to claim 9 wherein said recording layer has a thickness of more than 3µm and is ink receptive and wherein image-wise exposure proceeds through said hardened hydrophilic surface layer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/00118

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B41C1/055 B41M5/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 B41C B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 160 396 (IMPERIAL CHEMICAL INDUSTRIES PLC) 6 November 1985 see page 2, line 23 - line 32 see page 4, line 19 - line 27 see page 6, line 30 - line 34 see page 7, line 25 - line 29	1-10
X	EP,A,0 164 128 (H.A.FROMSON) 11 December 1985 see page 3, line 11 - page 5, line 14 see page 9; table 2	1
X	FR,A,2 258 649 (SCOTT PAPER COMPANY) 18 August 1975 see page 2, line 4 - page 3, line 5; claims 1,4; example 4	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
8 March 1994	[illegible]
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Bacon, A A J Bacon

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/00118

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0160396	06-11-85	DE-A-	3584788	16-01-92
		US-A-	4711834	08-12-87
		US-A-	4626493	02-12-86
EP-A-0164128	11-12-85	CA-A-	1249944	14-02-89
		JP-A-	61018960	27-01-86
		US-A-	4731317	15-03-88
FR-A-2258649	18-08-75	CA-A-	1049312	27-02-79
		DE-A,B	2500907	24-07-75
		GB-A-	1492070	16-11-77
		JP-A-	50102401	13-08-75
		JP-B-	51006568	28-02-76
		US-A-	4132168	02-01-79